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Water Dimer Rotationally Resolved Millimeter-Wave Spectrum Observation at Room Temperature

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Water dimers $(H_2O)_2$ are believed to affect Earth's radiation balance and climate, homogeneous condensation, and atmospheric chemistry. Moreover, the pairwise interaction which binds the dimer appears to be of paramount importance for expounding a complete molecular description of the liquid and solid phases of water. However, there have been no secure, direct observations of water dimers at environmentally relevant temperatures despite decades of studies. We report the first unambiguous observation of the dimer spectrum recorded in equilibrium water vapor at room temperature.

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The role of water dimers in atmospheric processes remains controversial despite decades of effort. Dimers are thought to affect Earth's radiation balance and climate [1–4], homogeneous condensation [5], and atmospheric chemistry [6]. All these processes occur at ambient conditions in thermodynamic equilibrium. However, there are no secure, direct observations of water dimers in equilibrium at environmentally relevant temperatures either in the atmosphere itself or in laboratory. Herman and Saykally [7] editorialized that "Yes, the water vapor dimer is very likely to be present in our atmosphere and yes it is expected to contribute a profound fraction of the radiation budget; beware of fakes when searching for evidence of complexes and make sure that monomer contributions are accounted for up to the latest details, including all refinement in the line profile investigation."

Numerous low-temperature spectroscopic studies of the water dimer have been conducted in supersonic molecular beams (Refs. [8–10] and references therein), in matrices [11], and in helium nanodroplets [12]. These studies provide information on the structure and spectrum of the water dimer, including fine details of its internal dynamics. However, such studies cannot provide answers about the atmospheric abundance of the dimer in ambient conditions. The ultimate aim of such a study would be direct observation of the water dimer in ambient conditions but a key first step is the observation of its spectrum in equilibrium, room temperature water vapor.

The difficulty of observing water dimers either *in situ* in the atmosphere or in ambient laboratory conditions is well documented [7]. In the infrared, the main problem is the natural overlap of most dimer vibrational-rotational bands with water monomer ones, which are more intense by about 3 orders of magnitude. One approach [13] is to subtract the line-by-line calculated monomer spectrum from the total experimental absorption in water vapor to obtain broad unresolved spectral bands. Interpretation of these bands is ambiguous, and indirect ways such as temperature and/or pressure dependences are used as evidence of their dimeric origin.

Several attempts have been made to observe single features of the vibrational-rotational spectra of the dimer. Enormous inhomogeneous broadening of the dimer spectrum under ambient conditions prevented laboratory observation of the characteristic Q branch observed in cold molecular beams [14]. Gebbie *et al.*'s claimed observation of water dimers in Earth's atmosphere [15] has never been confirmed. More recent atmospheric observations of the water dimer vibrational overtone around 750 nm were made by Pfeilsticker *et al.* [16]. The results were criticized by Kassi *et al.* [17] who attributed the findings to weak monomer absorptions. Shillings *et al.* [18] reinvestigated the 750 nm region using both improved experimental apparatus and water monomer line list. They observed no absorption features other than those attributable to the water monomer in experiments performed on water vapor samples containing dimer concentrations up to an order of magnitude greater than those expected in Earth's atmosphere.

To avoid the risk of erroneous dimer detection in the rich spectrum of water vapor spectrum, a search should look not for a single feature but for a discrete spectral series that can be established unambiguously as belonging to the dimer. The rotational spectrum of the dimer is an appropriate candidate for this. The discrete nature of the dimer rotational spectrum and its potential impact on the atmospheric absorption was first considered by Viktorova and Zhevakin (see Ref. [19] and references therein). The rotational spectra of the dimer and the monomer are very different due to their differences in mass and symmetry, which means that separation of the spectra represents no difficulty. Estimations suggested that the intensity of the "end-over-end" rotation dimer lines should be sufficient for their observation using existing spectrometers [20]. This was confirmed by results of the most accurate quantum mechanical calculations of the far-infrared and millimeter dimer spectrum [21].

This *ab initio* approach was used to calculate separate components of the dimer spectrum, which demonstrated the potential existence of a discernible spectral series of discrete dimer features [22]. This series corresponds to rotational transitions of E_1 type, which are only weakly affected by the fast tunneling motion in the dimer and form an almost equidistant rigid rotor pattern. The frequencies of the most intense lines corresponding to such transitions, namely, $J + 1 \leftarrow J$, $K = 0$ series in the ground vibrational state, can be easily calculated as the rotational spectrum of a diatomic molecule formed by two heavy oxygen atoms with effective rotational and centrifugal constants $B_{\mathrm{eff}} = 6160.6011(21)$ MHz, $D_J = 0.050079(91)$ MHz [9] determined from several first rotational transition frequencies accurately measured in cold beams [9,10,23]. The accuracy of the predicted frequencies for lines ranging from $J = 8$ up to $J = 11$, which are the most appropriate for observation of the ambient spectrum, amounts to a fraction of a MHz, much less than the expected width of the corresponding spectral features. Conversely, the accuracy of the predicted *ab initio* line frequencies is lower, but these calculations provide the intensity of the predicted spectrum, its general pattern, and the relatively uniform background absorption due to other dimer rotational transitions [22].

The *ab initio* calculations also show that the discrete rotational features of the dimer spectrum are too broad to be observed using the usual high resolution spectrometers operating at low pressures. Only resonator spectrometers, where the absorption is measured as the change in the resonator quality factor after it is filled with the sample, appear capable of observing this weak spectrum. We have developed a resonator spectrometer operating in the millimeter-wave band with a high-Q Fabry-Perot resonator and fast precise phase-continuous scanning of the radiation frequency [24] and successfully used it for accurate studies of broad atmospheric lines and continuum absorption. At present, this spectrometer has one of the highest available sensitivities. The spectrometer and the experimental procedures used are described elsewhere [24,25]. Specific experimental details are given in the Supplemental Material [26].

Figure 1 presents the observed spectrum of water vapor recorded at a pressure of 13 Torr and a temperature of 296 K. The dimer spectrum was investigated by considering the difference between the total observed absorption and the monomer absorption. The latter one was calculated as a line-by-line sum of spectra due to the four major water isotopologues in natural abundances. All significant transitions with frequencies up to 1 THz reported in HITRAN [27] were included in the list. The monomer within 100–150 GHz shows just a few weak, narrow lines belonging to the partially deuterated water molecule HDO and to the excited bending state of $H_2{}^{16}O$ (Fig. 1, bottom trace). Note that the monomer contribution to the total absorption is small.

Dimer absorption was modeled as a sum of two functions. The first one represents the E_1-type rotational transitions as a sum of Lorentzian profiles located at the frequencies predicted from the rotational constants of the $J + 1 \leftarrow J$, $K = 0$ series with J ranging from 0 to 20 with relative intensities given by the *ab initio* calculations. The second function is a low-order polynomial that accounts for the other dimer transitions. The model absorption fitted to the observed spectrum is also shown in Fig. 1. It can be seen that the model reproduces the observed spectrum very well. Observation of four consecutive members of a nearly equidistant rotational spectral series separated by approximately $2B_{\mathrm{eff}}$ and centered at positions predicted from supersonic beam measurements makes the assignment of these features to the water dimer reliable and unambiguous.

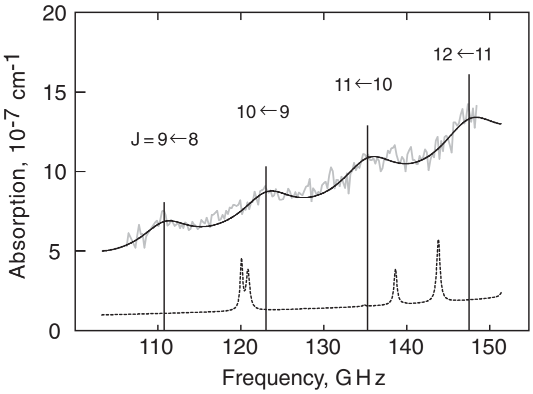

FIG. 1. Observed water vapor spectrum after monomer contribution subtraction (broken line), calculated water monomer spectrum (smooth dotted line), and model dimer absorption (smooth solid line). Vertical bars show positions of the $J + 1 \leftarrow J$, $K = 0$, E_1-type dimer rotational lines.

This experimental spectrum is fully reproducible (see the Supplemental Material [26]).

Figure 2 compares the observed spectrum with the calculated one and with other types of water vapor absorption under the same conditions. The observed spectrum [Fig. 2(a)] differs from the *ab initio* one [Fig. 2(b) upper trace] as experimental rotational peaks of the dimer are broader than the calculated ones. Note that the shape of the spectrum results from merging thousands of pressure broadened individual dimer lines corresponding to different rotational, rotational-tunneling, and rotational-vibrational transitions. The calculated peaks become comparable with the observed ones if the individual line width is increased by about a factor of 3.8. However, interpretation of the excess width of the peaks as collisional broadening of individual lines appears improbable because it would require water dimer broadening parameter in water vapor of about 150 MHz/Torr, which exceeds all known pressure-broadening parameters for lines of strongly polar molecules. Ascribing the broader peaks to contributions from metastable dimers also seems improbable because it would require most of the dimers to be metastable, while calculations [21] supported by agreement with experiment [28] show that in ambient conditions only a minority of

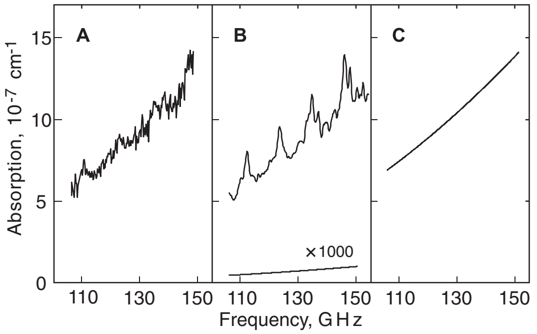

FIG. 2. The observed dimer spectrum (a). The *ab intio* calculated [21] dimer spectrum [(b) upper trace]. The water vapor continuum absorption measured in moist nitrogen [28] at atmospheric pressure (c). The calculated collision-induced absorption [32] [(b) lower trace], the absorption is shown multiplied by factor of 1000 to make it visible). All spectra correspond to water vapor at 13 Torr and 296 K.

the dimers are metastable. The other evidence against the involvement of metastable dimers is the symmetry of the peaks and the fact that they are centered at frequencies predicted from the observed, low temperature rotational frequencies.

The most likely explanation for the difference between the experimental and the calculated spectra is the symmetric top approximation used in the calculations [21,22]. In reality, the dimer is a prolate, slightly asymmetric, and very nonrigid rotor; however, its spectrum cannot at present be calculated without simplifications. The observed peaks monitor water dimer rotational transitions not only from the ground vibrational state but also in low-frequency vibrational states. Many of such states are thermally populated enough to contribute to the observed spectrum at ambient temperature [21,29].

The amplitudes of the observed [Fig. 2(a)] and *ab initio* [Fig. 2(b) upper trace] dimer spectra are in a good agreement. Moreover, analysis of integrated absorption of characteristic peaks in the observed and calculated spectra shows that they coincide within experimental accuracy (see the Supplemental Material [26]). This implies similar coincidence for the remaining, quasicontinuous background absorption. Comparison of the observed and calculated spectra allows estimation of the dimer relative abundance as about 1.0×10^{-3}. The observed spectrum is also in good agreement with measurements of the H_2O self-continuum absorption in a mixture of water vapor with nitrogen at atmospheric pressure [28], which is shown in Fig. 2(c). The coincidence of these three spectra supports the conclusion [21,28,30,31] that, in ambient conditions, dimer absorption alone is responsible for the observed atmospheric water vapor continuum in the millimeter-wave range. We note that the contribution of collision induced absorption in this region is negligible in our experimental conditions, as shown by the results of calculations [32] [Fig. 2(b) lower trace].

The agreement between the observed and calculated spectra also supports the water dimer equilibrium constant determined *ab initio* [33] and used in the spectral calculations. The value of this constant remains poorly determined in ambient conditions (see Ref. [18] for a recent review). An accurate experimental measurement could be achieved by recording the present spectrum with an improved signal-to-noise ratio; this can only be achieved with increased spectrometer sensitivity.

The observation of the spectrum of water dimer at room temperature opens the way for studies of the role of the water dimer in natural processes important for atmospheric chemistry and climate studies. Moreover, detailed study of the dimer equilibrium spectrum in extended frequency, temperature, and pressure ranges, supported by the corresponding *ab initio* calculations, will further our understanding of the water dimer. The pairwise interaction that binds the dimer appears to be of paramount importance for expounding a complete molecular description of the liquid and solid phases of water [34].

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